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CHEMICAL COMPOSITION AND MORPHOLOGY OF OXIDIC CERAMICS AT FILTRATION OF STEEL DEOXIDISED BY ALUMINIUM

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Composition and morphology of filter ceramics were investigated during filtration of steel deoxidised by aluminium. Filtration was realised with use of filters based on oxidic ceramics Cr_2O_3, TiO_2, SiO_2, ZrO_2, Al_2O_3, $3Al_2O_3{\cdot}2SiO_2$ and $MgO{\cdot}Al_2O_3$. It was established that change of interphase (coating) occurs during filtration of steel on the surface of capillaries of ceramics, where content of basic oxidic component decreases. Loss of oxidic component in the coating is replaced by increase of oxides of manganese and iron and it is great extent inversely proportional to the value of Gibbs' energy of oxide, which forms this initial basis of ceramics.

Key words: filtration of steel, ceramic filters, interphase reactions, thermodynamic stability of filter

Kemijski sastav i morfologija oksidne keramike tijekom filtriranja aluminijem deoksidiranog čelika. Sastav i morfologija filterske keramike ispitivana je tokom filtriranja aluminijem deoksidiranog čelika. Filtriranje je provedeno filterima izrađenim od oksidne keramike Cr_2O_3, TiO_2, SiO_2, ZrO_2, Al_2O_3, $3Al_2O_3{\cdot}2SiO_2$ te $MgO{\cdot}Al_2O_3$. Utvrđeno je kako tijekom filtriranja do promjene međufaze (stvaranja sloja) dolazi na kapilarnim površinama keramike, u kojima se udio temeljne oksidne komponente smanjuje. Taj gubitak nadomješten je manganskim i željeznim oksidom i uglavnom je obrnuto proporcionalan vrijednosti Gibbsove energije oksida, koji čini osnovu keramičke tvari.

Ključne riječi: filtriranje čelika, keramički filteri, reakcije međufaze, termodinamička stabilnost filtera

INTRODUCTION

On the boundary of any two phases a transition region is formed, designated as *interphase*, the composition of which is not identical with composition of the internal part of any of two phases. This transition region – *interphase* – is formed by effect of surface forces, given by the character and composition of both contacting phases, and its thickness is usually of the order of molecular dimension. If this interphase is being enriched as a result of influence of surface forces by certain substance due to its concentration inside the phase (for example solid phase), such accumulation of the given substance at the contact of two phases is called *adsorption*.

Among the physical forces that cause adsorption in solutions particularly the *capillary* forces take their effect, whereas the filtered molten steel can be regarded as multi-component liquid solution. Ceramic filter is characterised always by certain porosity. If we take into account the fact that relative surface of solid phase increases with its porosity, then the higher is porosity of ceramic filter, the more distinct is manifestation of phenomena related to adsorption at flow of molten steel through ceramic filter. In this case we distinguish *physical* adsorption, which takes place predominantly at lower temperatures, and *chemical* adsorption, which manifests itself intensively at high temperatures.

When the melt enters the ceramic filter, the temperature of which is in the first phase close to the temperature of surrounding atmosphere, it is possible to expect effect of *physical* adsorption, and gradually with increasing temperature of ceramic filter up to the value of the steel flowing through the filter, i.e. 1600 °C, it is possible to expect effect of *chemical adsorption.* Adsorption at these conditions is already connected with physical-chemical reactions between the molten steel flowing through the filter, non-metallic particles, i.e. inclusions in steel and oxidic ceramics of the relevant filter.

Adsorption effects can take place at the boundary of solid porous surface of ceramics, which is in contact with molten steel flowing through the filter capillary thanks to characteristic distribution of flow rate of molten steel through the capillary hole [1-4]. The reason is that at laminar and turbulent flow through the filter capillary the flow rate w of molten steel on the interphase boundary of the type (solid phase / molten metal) is approaching the zero value, which means that molten steel can here penetrate the porous surface of ceramics, which gradually melts and mixes with melt of filtered steel.

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Highly viscous coating is formed on the surface of capillaries. Its composition is determined by intensity and extent of physical-chemical reactions between the melt of filtered steel contaminated by non-metallic inclusions and surface of filter capillaries.

Consequences of reactions between the melt of filtered steel and surface of ceramic filter capillaries were experimentally investigated altogether in eight types of ceramic filters with direct holes with different ceramic basis. In this case low-carbon unalloyed steel was filtered that was molten in an induction furnace, which was first deoxidised by aluminium with addition of calcium.

Special series of ceramic filters with direct holes was manufactured by the company KERAMTECH Žacléř, s.r.o. The company produced altogether seven filters of the type 0220 made of oxidic ceramics – Cr_2O_3, TiO_2, SiO_2, ZrO_2, Al_2O_3, $3Al_2O_3{\cdot}2SiO_2$, $MgO{\cdot}Al_2O_3$. To this series of filters another filter was added, namely filter RK5 on mullitic basis, produced also by the company KERAMTECH Žacléř, s.r.o., which was designated for filtration of steel [5]. Filters had the following basic parameters: filter diameter 60 mm, hole (capillary) diameter 5,5 mm, number of holes 37 and height of the filter 7 mm. Layout of location of individual ceramic filters into the feeder system during filtration of steel was described and illustrated in detail in the work [6].

After filtration of steel with use of individual types of filters and after solidification of steel in the feeder system, the ceramic filters were cut in direction from capillary axes, and metallographic polished specimens were prepared on surfaces of sections. These specimens were used for detailed analysis of chemical composition of slag coating formed during filtration on the surface of individual filter capillaries, as well as basic chemical composition of ceramic mass of the used filters at the points, which were not in contact with molten steel during filtration.

CHANGES OF CHEMICAL COMPOSITION IN THE SURFACE LAYER OF CAPILLARIES AT FILTRATION OF MOLTEN STEEL

Changes of chemical composition of filter capillaries (channels), through which flowed molten steel were experimentally investigated in detail in relation to the final deoxidation by aluminium with addition of calcium. Low thermodynamic activity and low content of oxygen corresponds to deoxidation by aluminium and calcium after accomplished final deoxidation.

Results of measurement of chemical composition of changes in composition of surface layers of capillaries of ceramic filters after flow of molten steel were related to the original chemical composition of ceramics of filters, which was not in contact with the filtered melt. These results are summarised in the Table 1. A working term *coating* was used for designation of different composition of ceramic surface after filtration, i.e. for so called *interphase*. The Table 1 shows the *difference* in chemical composition of *ceramics/coating* (i.e. the difference between the initial composition of ceramics and chemical composition of the coating), where symbol (–) means decrease and symbol (+) means increase of oxidic component of ceramics in the coating on its surface in wt.%. Bases of the used ceramics are printed in the Table 1 in bold characters.

The following main conclusions follow from comparison of the initial chemical composition of filter ceramics and coatings:

- Characteristic feature of the steel deoxidised in the final stage by aluminium is the fact, that during its filtration the initial chemical composition of the basic oxidic ceramics on the surface of capillaries distinctively changes in the whole series of eight filters.
- On the surface of capillaries an *interphase* is formed, i.e. coating, layer of oxides, in composition of which during filtration the content of the component that formed the basis of original oxidic ceramics of the filter decreases.
- Loss of oxidic component, which formed basis of initial ceramics is in the coating replaced in the whole series of eight filters particularly by increases of oxides of manganese and also iron.
- It is remarkable that percentage decreases of the oxide forming the basis of initial ceramics are nevertheless in the coating in great extent inversely proportional to the absolute value of the Gibbs' energy of the oxide, which forms this initial basis of ceramics. In other words, the more thermo-dynamically stable is the oxide forming the initial basis of filter ceramics, the smaller are its relative decreases in the coating, but also the smaller relative increases of the oxide of manganese and iron in the coating on the filter capillaries surface after filtration of molten steel.

Morphology of oxidic coating, formed during filtration on the surface of capillaries of filters made from individual oxidic ceramics, is illustrated by the series of photos of cross section of capillaries shown in the Figures 1 and 2. Graphical representation of decreases of basic ceramic basis of filters is shown in the form of diagram in the Figure 3.

It follows from the diagram in the Figure 3, that losses of initial ceramic basis in coating during filtration increase. Only in case of the filter based on ZrO_2 relative increase of portion of this initial basis in coating was detected. In the sequence of filters with ceramic basis $3Al_2O_3{\cdot}2SiO_2$, SiO_2 and Al_2O_3 the decreases of initial basis are small (low percentage) and mutually comparable. In case of the filter RK5 the loss of the initial basis is higher by an order (more than 10 wt.%), but losses in-

Table 1. **Changes of composition of ceramics on the surface of walls in the coating of filter capillaries: symbol (–) means decrease, symbol (+) means increase of oxidic component of coating ceramics on the surface.**

	wt.%										
Al_2O_3 1	MgO	**Al_2O_3**	SiO_2	P_2O_5	S	K_2O	CaO	TiO_2	Cr_2O_3	MnO	Fe_2O_3
ceramics	1,15	**75,02**	13,66	0,00	0,07	0,21	0,12	2,21	0,03	5,19	2,31
coating	1,24	**72,44**	10,18	0,00	0,01	0,07	0,11	3,41	0,10	7,88	2,09
difference	+0,09	**-2,58**	-3,48	0,00	-0,06	-0,14	-0,01	+1,21	+0,07	+2,69	+0,22
Cr_2O_3 2	MgO	Al_2O_3	SiO_2	P_2O_5	S	K_2O	CaO	TiO_2	**Cr_2O_3**	MnO	Fe_2O_3
ceramics	0,33	3,49	7,59	0,00	0,01	0,12	0,17	0,19	**84,04**	0,00	1,13
coating	1,52	19,83	34,28	0,00	0,08	0,12	0,32	11,62	**11,28**	18,17	2,83
difference	+1,19	+16,34	+26,69	0,00	+0,07	0,00	0,15	+11,43	**-72,76**	+18,17	+1,70
TiO_2 3	MgO	Al_2O_3	SiO_2	P_2O_5	S	K_2O	CaO	**TiO_2**	Cr_2O_3	MnO	Fe_2O_3
ceramics	0,33	12,66	12,78	0,00	0,00	0,28	0,10	**73,20**	0,02	0,04	0,62
coating	0,81	13,25	23,87	0,00	0,03	0,21	0,11	**31,13**	0,06	6,89	19,68
difference	+0,41	+0,59	+11,09	0,00	+0,03	-0,07	+0,01	**-42,07**	+0,04	+6,85	+19,06
ZrO_2 4	MgO	Al_2O_3	SiO_2	S	K_2O	CaO	TiO_2	Cr_2O_3	MnO	Fe_2O_3	**ZrO_2**
ceramics	0,98	13,84	15,46	0,00	0,35	0,88	2,26	0,02	7,02	1,25	**58,69**
coating	0,75	8,39	9,44	0,00	0,12	0,09	3,78	0,00	7,36	1,82	**68,27**
difference	-0,23	-5,45	-6,02	0,00	-0,23	-0,79	1,52	-0,02	+0,34	+0,57	**+9,58**
SiO_2 5	MgO	Al_2O_3	**SiO_2**	P_2O_5	S	K_2O	CaO	TiO_2	Cr_2O_3	MnO	Fe_2O_3
ceramics	0,32	9,35	**84,19**	0,00	0,09	0,80	0,17	0,34	0,11	0,00	4,64
coating	0,39	7,17	**82,92**	0,00	0,02	0,49	0,05	0,72	0,04	6,54	1,64
difference	+0,07	-2,18	**-1,27**	0,00	-0,07	-0,31	-0,12	+0,38	-0,07	+6,54	-3,00
Filter 6	MgO	**Al_2O_3**	**SiO_2**	P_2O_5	S	K_2O	CaO	TiO_2	Cr_2O_3	MnO	Fe_2O_3
ceramics	1,07	**69,12**	**27,12**	0,00	0,03	0,72	0,18	0,34	0,00	0,02	1,43
coating	1,33	**52,15**	**28,53**	0,00	0,04	0,48	0,15	3,54	0,06	10,70	3,06
difference	+0,26	**-16,97**	**+1,41**	0,00	+0,01	-0,24	-0,03	+3,20	+0,06	10,68	1,63
Filter 7	MgO	**Al_2O_3**	**SiO_2**	P_2O_5	S	K_2O	CaO	TiO_2	Cr_2O_3	MnO	Fe_2O_3
ceramics	0,88	**65,58**	**32,01**	0,00	0,03	0,14	0,09	0,30	0,09	0,00	0,90
coating	0,97	**60,43**	**26,00**	0,00	0,03	0,21	0,16	1,29	0,04	8,99	1,90
difference	+0,09	**-5,15**	**-6,01**	0,00	0,00	+0,07	+0,07	+0,99	-0,05	+8,99	+1,00
Filter 8	**MgO**	**Al_2O_3**	SiO_2	P_2O_5	S	K_2O	CaO	TiO_2	Cr_2O_3	MnO	Fe_2O_3
ceramics	**25,11**	**63,25**	9,93	0,00	0,00	0,23	0,05	0,33	0,03	0,00	1,11
coating	**20,87**	**32,44**	14,22	0,00	0,00	0,02	0,31	0,31	0,02	1,97	30,11
difference	**-4,24**	**-30,81**	+4,29	0,00	0,00	-0,21	+0,26	-0,02	-0,01	1,97	29,00

Notes: Filter 6 = (RK5) – Filter manufactured industrially at the company KERAMTECH Žacléř, s.r.o. on mullitic basis, designated for filtration of steel; Filter 7 – ($3Al_2O_3 \cdot 2SiO_2$); Filter 8 – ($MgO \cdot Al_2O_3$); initial basis of oxidic ceramics is highlighted in the table by bold characters.

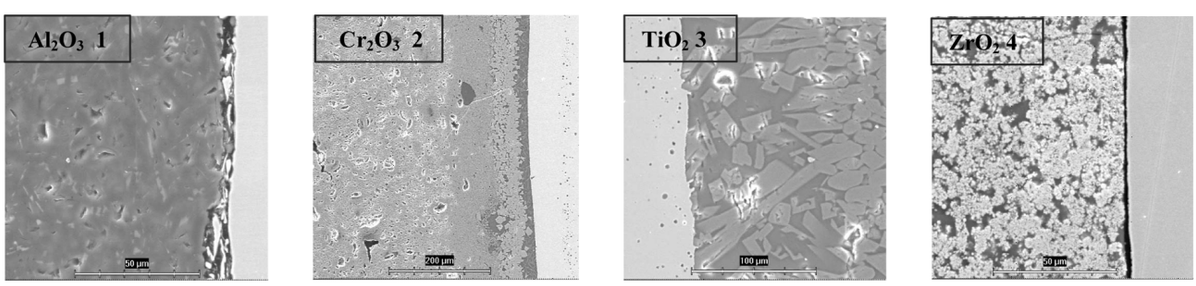

Figure 1. Cross sections of capillaries of filters Nos. 1, 2, 3 and 4 (non-etched)

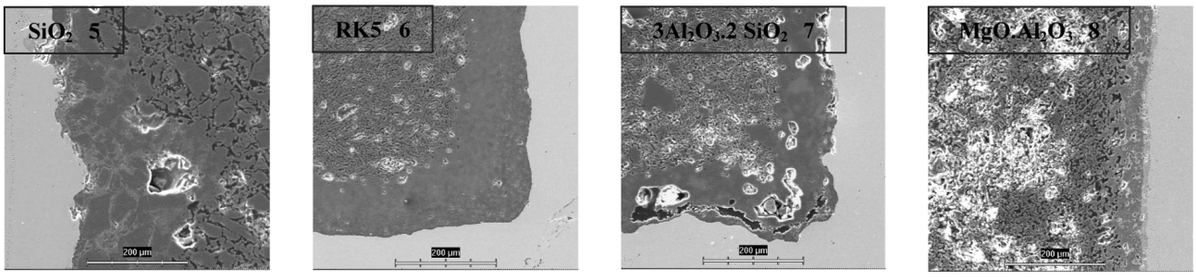

Figure 2. Cross sections of capillaries of filters Nos. 5, 6, 7 and 8 (non-etched)

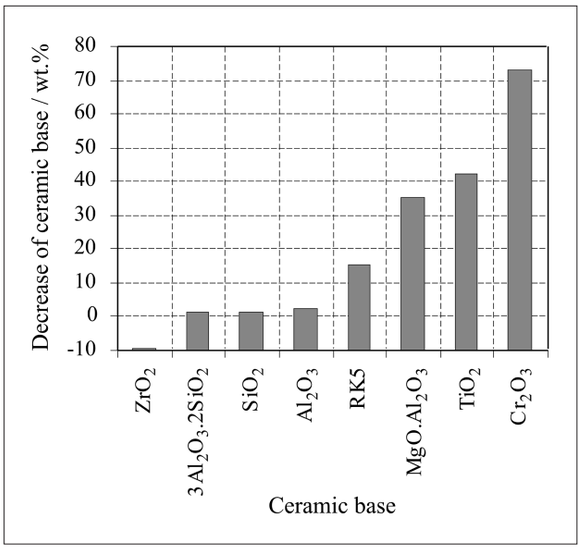

Figure 3. Decreases of ceramic basis of filters in coating during filtration of molten steel

crease substantially in filters based on $MgO{\cdot}Al_2O_3$ and TiO_2, and the biggest decreases were observed in the filter Cr_2O_3, the basic oxide of which has the smallest thermo-dynamic stability (i.e. the lowest value of Gibbs' energy). Estimate of Gibbs' energy (free enthalpy) of oxides of initial ceramic basis made with use of literature [7] is given in the Table 2.

CONCLUSION

If we compare thermodynamic stability of initial oxidic ceramic basis according to the Table 2, we can see that it decreases in the sequence of the filters $3Al_2O_3{\cdot}2SiO_2$, $MgO.Al_2O_3$, RK5, Al_2O_3, SiO_2, TiO_2, ZrO_2 and Cr_2O_3, whereas losses of this basis in coating of capillaries are in the sequence ZrO_2 (increase), $3Al_2O_3{\cdot}2SiO_2$, SiO_2, Al_2O_3, RK5, $MgO{\cdot}Al_2O_3$, TiO_2, and Cr_2O_3. It is obvious that apart from influence of overall lower thermo-dynamic stability of oxidic ceramics also other factors participate in changes of chemical composition of coating of capillaries, i.e. on the increase of portion of oxides of manganese and iron in the coating (Table 1). These factors comprise softening and melting temperature of the given oxidic ceramic basis of the filter, its porosity and also reactivity in relation to the melt of filtered steel flowing through the capillaries. From practical viewpoint it is possible to consider the first five filters in the Figure 3 as the filters, the oxidic basis of which has acceptable filtration stability, while remaining three filters, i.e. $MgO{\cdot}Al_2O_3$, TiO_2, and Cr_2O_3 appear to be unsuitable for filtration of steel.

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Table 2. **Estimate of Gibbs' energy (free enthalpy) of initial basis of oxidic ceramics of filters - according to the literature [7]**

Filter No.	Type of filter	$-\Delta G_{MxOy}$ /kJ/(mol M_xO_y)	$-\Delta G_{MxOy} \cdot (M_xO_y)_{wt.\,fraction\ initial}$ /kJ/(mol O) · (wt. fraction)	$(M_xO_y)_{wt.\%-loss}$/wt.%
1	Al_2O_3	1141,5 (380,50) [1)]	**285,45**	**2,58**
2	Cr_2O_3	729,8 (243,26) [1)]	**204,43**	**72,76**
3	TiO_2	651,7 (325,50) [1)]	**238,27**	**42,07**
4	ZrO_2	802,1 (401,05) [1)]	**235,37**	**-9,58**
5	SiO_2	640,8 (320,39) [1)]	**269,73**	**1,27**
6	RK5	by composition [2)]	**349,94**	**15,56**
7	$3Al_2O_3{\cdot}2SiO_2$	by composition [3)]	**352,08**	**1,16**
8	$MgO{\cdot}Al_2O_3$	by composition [4)]	**351,79**	**35,05**

Notes: [1)] reduced to mol of oxygen; [2)] determined by the measured chemical composition of the oxides Al_2O_3 and SiO_2 in the filter RK5 – see the note at the Table 1; [3)] determined by the oxides Al_2O_3 and SiO_2 with reduction to mol O; [4)] by the oxides $MgO.Al_2O_3$ to mol O; $-\Delta G_{MgO}$ = 439,7 kJ/mol [6].

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Note: The responsible translator for English language is B. Šandera, Czech Republic.